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Low-Temperature Evolution of Hydrocarbon Gases From Coal

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LOW-TEMPERATURE EVOLUTION OF HYDROCARBON GASES FROM COAL[1]

by

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ABSTRACT

Hydrocarbon gases, primarily methane but also the C_2 through C_5 paraffins, the C_2 and C_3 olefins and possibly the C_4 and C_5 olefins, are byproducts of coal formation. Although it is generally believed that coal formation occurred at temperatures below 200° C, most experimental work on gas formation from coal has been performed at temperatures between 200° and 1,000°C. The objective of this Bureau of Mines experiment was to determine if observable changes in the gases from coal could be produced at temperatures below 200° C in relatively short periods of time. The experiment involved heating coal samples from six coalbeds at constant temperatures and analyzing evolved gases. The composition of the gases at three temperatures was compared. At 35° C, over 99 pct of the gas is methane; at 125° and 150°, methane constitutes approximately half of the hydrocarbon gas. Isobutane and pentane are the predominant higher hydrocarbons at temperatures between 100° and 150° C.

INTRODUCTION

Coal is an essential source of energy for the present and the future. However, to efficiently utilize our coal resources, it will be necessary to significantly improve the safety of coal mining. The continual release of methane from coal and the potential formation of explosive mixtures in the mine atmosphere comprise one of the hazards associated with coal mining. In its efforts to improve methane control, the Bureau of Mines has conducted research in the application of advanced mining technology, the development of reliable monitoring instrumentation, and the determination of physical, geological, and geochemical factors that affect the retention and release of gas in coal.

It has been known, probably since the beginning of mining, that coal contains a combustible gas, sometimes in sufficient quantity for the coalbed

[1]The data in this publication were submitted as a thesis to the University of Pittsburgh in partial fulfillment of the requirements for the degree of Master of Science.

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to serve as a source of natural gas (41).[3] It was originally believed that the hydrocarbon gas in coal consisted entirely of methane. Approximately 50 years ago ethane was also detected in coalbed gases, but was attributed to contamination from natural gas horizons below the coal (38). With the development of gas chromatography, a comple analysis of coal gases became possible. The number of analyses performed to date is relatively small, but they have established that the gas from coal contains the C_2 through C_5 paraffins, the C_2 and C_3 olefins, and possibly the C_4 and C_5 olefins in addition to methane, carbon dioxide, oxygen, nitrogen; hydrogen and helium also occur in coal gas in varying amounts (17, 19, 24-25, 30).

Current ventilation procedures can be successfully applied by treating the coal gas as methane alone. In future mine developments, it may be necessary to treat the gas as the multicomponent mixture it is. This would require more extensive knowledge of the formation and composition of hydrocarbon gases in coal. Although coal formation and the associated formation of hydrocarbon gases is believed to have occurred at temperatures below 200°C over very long periods of time (13, 44), most experimental studies of gas formation from coal have been performed at temperatures from 200° to 1,000° C (6, 16, 28, 35). Since coal decomposition occurs at temperatures above 400° C, it is possible that the gas produced during these investigations is substantially different from the gas produced during coalification.

The objective of the present experiment was to determine if observable changes in the gases from coal could be produced in short periods of time at temperatures below 200° C. The experimental method consisted of heating coal samples at a constant temperature and analyzing the gases evolved. The composition of gases produced at three different temperatures was compared for coal samples from six coalbeds. The results from this experiment cannot be used to elucidate either the mechanism or kinetics of gas production. The method does not permit making a distinction between desorbed and formed gases. However, the results of this experiment demonstrate that the gas evolved from coal at temperatures below 200° C includes saturated and unsaturated hydrocarbons in addition to methane and that the composition of the gas is related to temperature. The low-temperature evolution of a complex gas mixture from coal, as shown in this and other studies (43, 45) supports the theory that hydrocarbon gas formation during coalification cannot be described by a simple demethanation mechanism.

FORMATION AND RETENTION OF HYDROCARBON GASES IN COAL

Hydrocarbon gases, primarily methane but also most of the C_2 through C_5 paraffins and olefins, are byproducts of coal formation. Coalification is that portion of the carbon cycle by which a series of biochemical and geochemical reactions transform plant material into a combustible solid (fig. 1). The rank designations lignite, brown coal, high-, medium-, and low-volatile bituminous coal, and anthracite are roughly equivalent to different stages in a sequential transformation from low-rank to high-rank coals. The

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

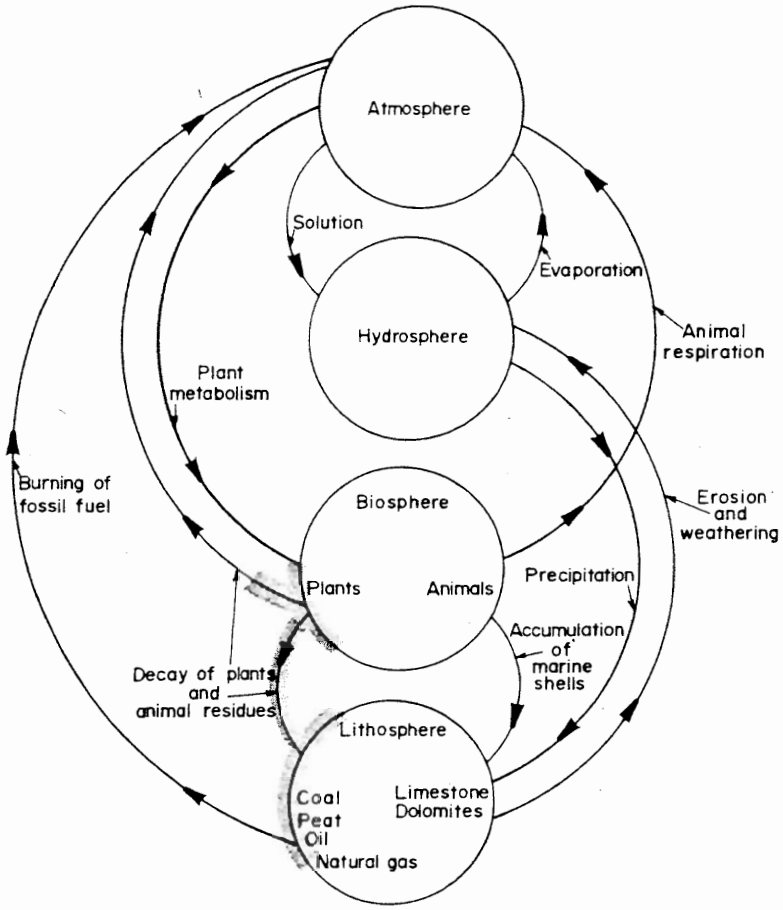

FIGURE 1. - Carbon cycle.

progenitors, the environment of deposition, the degree of metamorphism, and postdepositional history are factors that influence the present condition of a coalbed.

Coalification begins with a biochemical stage, during which plant materials are partially decomposed, humic materials are formed, and peat accumulates. For the formation of peat [defined as an unconsolidated, hydrophillic, carbonaceous sediment (37)], abundant plant materials, a suitable climate, areas for accumulating deposits of plant residues, and a means of preserving the carbonaceous sediments are required. Hydrocarbon gases produced during the biogenic stage include methane and trace amounts of ethane, ethylene, propane, propylene, the butanes, and pentanes. The gases are retained by adsorption on the peat. There is evidently no preferential concentration of the higher hydrocarbons in the peat deposit (20). Inundation by water and the deposition of inorganic sediments usually terminate the development of the peat bog and initiate the geochemical phase of coalification.

The geochemical stages of coalification can be described as a series of chemical reactions involving an increase in the aromatic character of the coal and the loss of hydrogen, oxygen, and some carbon (12, 14, 23). After the peat is removed from the biosphere, increasing overburden pressure compresses and desiccates the sediment. It has been estimated that between 10 and 20 ft of peat are eventually compressed to 1 ft of coal (2). Moisture content decreases from between 88 to 97 pct for peat to 20 pct for lignite as the concentration of humic acids increases. The humic acids are a group of polycondensed aromatic compounds with aliphatic side chains containing active methoxyl, carboxyl, and carbonyl groups. During coalification, removing or closing the side chains leads to an increase in aromatic content. The concentration of humic acids diminishes in more mature brown coals and becomes negligible in bituminous coals because the humic acids are oxidized to neutral compounds (27). The transition from lignite to bituminous coals is characterized by the removal of aliphatic side chains containing oxygen.

The transition from high-volatile to medium-volatile bituminous coals involves the removal of methyl and methylene groups. Aromatic clusters grow larger and form lamellae oriented parallel to the bedding plane (42). During diagenesis to the low-volatile stage, waxy and resinous material are incorporated into the coal. In low-rank coals, extractable paraffinic hydrocarbons show an odd carbon number preference; the distribution of odd to even carbon numbers becomes more nearly equal in higher rank coals, the change being a function of the degree of diagenesis (5). The formation of anthracite involves ring condensation and the growth of large aromatic clusters with a graphitelike structure. At this stage, the coal is composed of very large micelles in a more or less ordered arrangement (44).

The elemental ratios of carbon to hydrogen and carbon to oxygen change with rank. With an increase in rank, the aliphatic H/C ratio decreases while the aromatic H/C ratio increases. The proportion of aromatic to aliphatic carbon also increases (10, 29). Early in the coalification sequence, infrared spectra shows a decrease in absorption due to stretching bands, particularly the hydroxyl and eith linkages. There is a decrease in absorption due to aliphatic carbon and hydrogen, including the elimination of carbonyl groups, and an increase in aromatic character due to the growth of polynuclear condensed ring structures (23).

Pressure, temperature, and time influence the coalification reactions. In the early stages of coal formation, static vertical pressure, due to the weight of overlying sediments, causes compaction, decreases in porosity, and loss of moisture in low rank coals (11). In higher rank coals, experimental data suggests that high pressure may either cause depolymerization (18) or an increase in the graphite structure due to ring condensation (33). During periods of post-depositional folding, coal is subject to horizontal or shear pressures caused by tectonic forces, and increases in rank can be related to folding or regional uplift (7, 40).

Temperature is generally considered to be the most important factor in the catalysis of chemical changes during coalification. Contact metamorphism, increased temperature with depth, and thermal conductivity of adjacent rocks, which relate the degree of coalification to temperature, indicate that coal-forming reactions probably occurred below 200° C. Even at this relatively low temperature, estimated rates of reaction could produce all coals through anthracite in geologically reasonable periods of time (13). The length of time a coal is exposed to a particular temperature affects the degree of rank attained, a long time at a low temperature being equivalent to a short time at a higher temperature (42).

Based on changes in elemental composition, Mott proposed gaseous products for changes in rank (31). By using the decrease in the percentage of C, H, and O per the net increase in fixed carbon, Mott calculated the relative amounts of CH_4, CO_2, H_2O, and H_2 that could possibly be formed during transitions to higher rank (table 1). Even with this simple approach and without including higher molecular weight hydrocarbons, more than

one set of reaction products is usually possible for each transition. No attempt was made to correlate the hypothetical reaction products with actual coalbed gases.

TABLE 1. - Gases produced during coalification (31)

Change		Gaseous reaction products
From--	To--	
Wood.....	Low-rank lignite.....	(i) $62H_2O + 9\ CH_4$ (ii) $64H_2 + 8CH_4 + CO_2$
Low-rank lignite.....	Low-rank bituminous.....	CO_2
Low-rank bituminous....	Medium-rank bituminous (a).	(i) $CH_4 + 8CO_2$ (ii) $10H_2O + 3CH_4 + 7CO_2$
Medium-rank bituminous (a).	Medium-rank bituminous (b).	(i) $6CH_4 + 4\ CO_2$ (ii) $5H_2O + 3CH_4 + CO_2$
Medium-rank bituminous (b).	Semianthracite.....	(i) $72\ CH_4 + 19CO_2$ (ii) $16H_2O + 64CH_4 + 11CO_2$
Semianthracite.....	Anthracite.....	$H_2O + 36CH_4$

In pyrolysis experiments on low-rank coals at temperatures between 150° and 1,000° C, the primary gaseous reaction products are carbon monoxide and carbon dioxide, although methane and higher hydrocarbons have been detected (16, 35). If no attempt is made to limit the amount of oxygen available during the experiment or to remove previously sorbed oxygen, oxidation will be the primary reaction (28). The oxidation reactions occur readily at all temperatures and could obscure the effect of low temperatures on the formation of hydrocarbon gases.

In the absence of definitive experimental evidence, proposed mechanisms of hydrocarbon gas formation during coalification must be considered speculative. However, there are several plausible mechanisms by which these gases could be produced during coal formation. Methane could be produced by removing alkyl side chains from aromatic molecules or by the decomposition of large straight-chain molecules. It could also form as straight-chain molecules are condensed to ring structures. These mechanisms account for observed increases in aromatic character with rank (4, 10). In low-rank coals, resins and waxes can be converted to mixtures of hydrocarbons; the decomposition of exinite also yields methane (5, 39). It has also been suggested that methane could form in a later stage, with ethane, ethylene, and hydrogen as the primary decomposition products. Methane would then be produced by a secondary reaction of these gases (45). If C_3 through C_5 hydrocarbons are also produced from the coal, they could decompose further to methane, with the coal acting as a catalytic surface. The reduction of carbon dioxide to methane is also possible. Carbon dioxide is believed to form early in the coalification process, probably by oxidation in the

Presence of occluded oxygen or by removal of carboxyl groups from low rank bituminous coals. With increased rank, the CO_2/CH_4 ratio decreases (9). Generally, the ratio of hydrocarbon gas to CO_2 is believed to increase with increased rank, and the percentage of higher hydrocarbons decreases (43).

The postdepositional history of the coal deposit strongly affects the amount of gas retained in the bed. Physically, coal is described as a solid colloid; that is, a solid, highly porous dispersion of discrete particles. The porosity of the coal is defined as the volume-percentage occupied by voids. Coal has two distinct pore systems: The macropore system, consisting of cracks and fractures; and the micropore system, similar to a molecular sieve structure. The micropores have an average diameter of 5 to 20 Angstroms and a very large surface area. Gas in coalbeds can exist as free gas in the macropore system or adsorbed on the surface of the micropores (26).

The adsorption of a gas on a solid may be either physical or chemical. Physical adsorption depends on van der Waal's forces between the adsorbent and the adsorbate, pressure, and temperature. It is exothermic ($\Delta H<10$ kcal/g) and produces adsorbed layers several molecules thick. Adsorption is appreciable only at temperatures below the boiling point of the adsorbate. Chemisorption results from a transfer of electrons between the solid and the adsorbed molecule. In effect, a chemical compound is formed at the surface of the solid. Chemisorbed layers are unimolecular. Chemisorption usually involves higher heats of adsorption ($\Delta H>20$ kcal/g). It is an activated process that proceeds at a finite rate, which increases rapidly with increased temperature. Adsorption can occur at temperatures above the boiling point of the adsorbate (3, 15). Both physical adsorption and chemisorption involve an equilibrium between adsorption and desorption.

Generally, the amount of adsorbed gas in coal increases with rank, and is influenced by pressure, temperature, degree of fracturing, and the permeability of the adjacent strata (34). Movement of gases out of the micropores follows Fick's Law of diffusion; if the diffusion coefficient is concentration-independent and adsorption obeys Henry's Law, then

$$q' = -DA\ dC/dL,$$

where q' is the volume flow rate, D is the diffusion coefficient, C is gas concentration, A is the area, and L is the path length (8, 32). Movement of gases is also controlled by the change in the adsorption-desorption equilibrium with changes in pressure. The number of desorbing molecules is related to the activation energy of desorption, the adsorbate density, the permeability and surface area of the solid, as well as the change in pressure (36). Flow through the fracture system is assumed to follow Darcy's Law:

$$dq/dt = K\Delta P/u,$$

where K is the fracture permeability, ΔP is the change in pressure, and u is the dynamic gas viscosity (34).

When coal is removed from a bed, gas emission depends upon the crack and pore structure and on the size of the coal particles. The total volume of gas given off increases with time, whereas the rate of gas emission decreases. For the total volume of gas given off,

$$V_t = A[1 - \exp(-t/t_o)^n] \text{ for } 1>n>0,$$

where V_t is the total volume of gas released per mass of coal, A is the initial gas content of the coal, t_o is a time constant, t is the time after the start of desorption, and n is an empirical factor. Generally, the volume of gas emitted increases rapidly then approaches a constant value, indicating a mechanism of pressure release followed by diffusion (1).

Gas exists in coal either adsorbed on the internal surface of the pores or free in the pores and fractures. The amount of gas retained or emitted depends on the temperature, pressure, degree of fracturing, permeability of the coal, and permeability of the adjacent strata. It is very difficult to completely degasify coal. Even "nongassy" coals contain small amounts of adsorbed hydrocarbons (21).

EXPERIMENTAL METHOD

The experimental method consisted basically of heating coal samples at a constant temperature and analyzing the gas produced. Seven samples of unweathered coal (table 2) were used. Lower rank coals were selected because these coals are usually high in volatile matter. Although volatile matter is not directly related either to the amount of gas contained in the coal or to the amount of hydrocarbon gas that can be produced from the coal, it should be an indicator of the ease with which hydrocarbon gases could be formed. To minimize the contribution of desorbed gases, all of the coal samples were obtained from "nongassy" mines; that is, mines that had no detectable gas emission.

TABLE 2. - Description of coal samples

Coal sample	Seam	Location	Moisture, pct	Ash, dry, pct	V.M. daf, pct	C daf, pct	H daf, pct	Rank
1	No. 1 (Rock Island).	Mercer Co., Ill...	13.9	17.5	48.4	74.2	5.9	HvCb
2	Laramie No. 3.	Weld Co., Colo....	21.0	4.8	41.3	76.3	4.8	Subbit.
3	Laramie No. 3.	Weld Co., Colo....	21.8	5.1	40.7	76.4	5.0	Subbit.
4	Mammoth.....	Monroe Co., Iowa..	14.1	10.8	52.2	83.0	5.9	HvCb
5	Uncorrelated bed.	Lucas Co., Iowa...	17.5	10.6	46.0	77.9	5.5	HvCb
6	Upper Freeport	Preston Co., W. Va.	1.5	9.4	35.4	86.2	5.2	HvAb
7	Pittsburgh....	Allegheny Co., Pa.	.9	6.6	41.4	84.0	5.6	HvAb

NOTE.--Daf = dry ash-free.

Each sample was crushed, the largest pieces being about 1/4-inch, then placed in a vacuum overnight at 90° C to remove some of the adsorbed gases. Ten grams of each crushed coal was placed in a Pyrex[4] test tube. The mouth of the test tube was covered with a double layer of Teflon tape. The remaining coal was sieved and samples taken from the 60/80- and minus 200-mesh fractions. All samples were prepared in triplicate.

In the presence of oxygen, coal can be oxidized at any temperature; the rate of oxidation increases with increased temperature. To minimize the extent of oxidation, each tube was flushed with nitrogen at 40 m./min for 5 min. The tubes, including a blank, were laid horizontally on racks in an oven at 125 ±2° C. To limit the amount of oxygen entering the tubes and to prevent the accumulation of hydrocarbon gases in the oven, nitrogen flow was maintained through the oven at a rate of 20 ml/min. A gas sample was obtained by inserting a 9-inch stainless steel needle attached to a disposable plastic syringe through the Teflon tape, to the far end of the tube and withdrawing 1-1/2 ml of gas. The hydrocarbon content of the gas was determined by gas chromatography, using a Poropak column and the flame ionization detector (22). One-half milliliter of gas was used to flush a standard 5/8-inch needle; then a 1-ml gas sample was injected into the chromatograph. The hydrocarbon composition was calculated by comparing the sample with a standard gas sample. The gas evolved from each sample was analyzed about once every 2 weeks, and results from the triplicate samples in each size range were averaged. After 45 days, the temperature of the oven was raised to 150° C, and sampling and analysis of the gas was continued at this temperature for 3 weeks. Single 10-gram samples of each coal in the 60/80 and minus- and minus 200-mesh fractions were prepared in a similar manner and placed in another oven at 35° C. Sampling and analytical procedures were the same as those used at the higher temperature. Samples were maintained at the low temperature for 2 weeks.

Because of its simplicity, this system had several inherent sources of error. Since pressure was not controlled, an increase in barometric pressure would force air into the sample tube. A change of 25 mm would equal 0.06×10^{-3} moles of gas or 2.8 pct. Similarly, if the temperature of the oven varied 5° C, the number of moles of gas in the tube would change 0.03×10^{-3} or 1.4 pct. Each time a gas sample was removed, 1.5 ml of air was drawn into the tube, diluting the gas 2.9 pct. Since the syringe used was not a precision gas-tight syringe, sample volume could be inaccurate as much as 3 pct. The total error was estimated at ±10 pct; the accuracy of the chromatographic analysis was 0.1 ppm; the quantitative sensitivity of the analysis was 0.01 ppm.

[4]Reference to specific brands of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

RESULTS

Each 1-ml sample of gas derived from the coals at 35° C (table 3) contained between 4 and 7 ppm total hydrocarbons of which 99.5 pct was methane with ethane and trace amounts of higher hydrocarbons. Ethylene was not detected in any of the samples. A combined value is given for propane and propylene because the chromatographic system used did not completely separate these compounds.

TABLE 3. - Average composition of hydrocarbon gases evolved from coal at 35° C, ppm

Coal sample	1	2	3	4	5	6	7
CH_4.....	4.2	3.8	3.7	6.9	3.8	4.8	4.8
C_2H_4.....	-	-	-	-	-	-	-
C_2H_6.....	.1	.01	.01	.02	.01	.02	Trace
C_3H_6.....	Trace	Trace	-	Trace	Trace	.02	Trace
C_3H_8.....							
Unidentified compound.....	-	-	-	-	-	-	-
$i\text{-}C_4H_{10}$.....	-	-	-	.05	Trace	-	Trace
$1\text{-}C_4H_8$.....	-	-	-	-	-	-	-
$n\text{-}C_4H_{10}$.....	-	-	-	Trace	Trace	Trace	Trace
C_5H_{12}.....	-	-	-	-	Trace	-	-
Total[2].....	4.3	3.81	3.71	6.97	3.81	4.84	4.8

[1]Sample numbers refer to those in table 2.
[2]Total hydrocarbon content of 1-ml sample.

NOTE.--Trace = < 0.01 ppm.

The gas produced from the coals at 125° C showed only small variations in composition over the 45-day period (3 to 15 ppm total hydrocarbons per 1-ml sample), with generally good agreement for the triplicate samples. The average composition of the hydrocarbon gas from each coal is given in parts per million per 1-ml sample in tables 4 through 6. Although total hydrocarbons derived from the various size fraction did not show large differences, generally more hydrocarbons were produced from the smaller size sample (fig. 2). Also, the percentage of methane in the hydrocarbon gas decreased with increasing surface area of the coal sample for the majority of coals. For example, in sample 1, at 125° C, the hydrocarbon gas from the unsized fraction contains 47 pct methane, the 60/80-mesh fraction contains 29 pct methane, and the minus 200-mesh fraction contains 21 pct methane. The ratio of methane to total hydrocarbons at 125° C decreased at least 20 pct relative to the ratio at 35° C, and the percentage of methane varied inversely with total hydrocarbons (fig. 3).

TABLE 4. - Composition of hydrocarbon gases, unsized fraction, 125° C

Coal sample..	1		2		3		4		5		6		7	
	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct
CH_4	5.8	46.8	7.3	50.0	7.1	39.6	7.7	37.2	6.2	78.1	5.1	71.6	9.7	41.8
C_2H_4	.5	4.0	.3	2.1	.7	3.9	1.2	5.8	.2	2.5	.02	.3	Trace	-
C_2H_6	.7	5.6	.5	3.4	.3	1.7	1.2	5.8	.1	1.3	.5	7.0	2.2	9.5
C_3H_6 / C_3H_8	.7	5.6	1.0	6.8	.7	3.9	1.7	8.2	.2	2.5	.3	4.2	1.3	5.6
Unidentified compound	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$i\text{-}C_4H_{10}$	2.5	20.2	1.5	10.3	1.4	7.8	4.0	19.3	.9	11.3	.9	12.6	4.7	20.3
$1\text{-}C_4H_8$	Trace	-	Trace	-	Trace	-	Trace	-	-	-	Trace	-	Trace	-
$n\text{-}C_4H_{10}$	.2	1.6	.2	1.4	.04	.2	.1	.5	.04	.5	-	-	.6	2.6
C_5H_{12}	2.0	16.1	3.8	26.0	7.7	42.9	4.8	23.2	.3	3.8	.3	4.2	4.7	20.3
Total[1]	12.4	99.9	14.6	100.0	17.94	100.0	20.7	100.0	7.94	100.0	7.12	99.9	23.2	100.1

[1]Total hydrocarbon content of 1-ml sample.

TABLE 5. - Composition of hydrocarbon gases, 60/80-mesh fraction, 125° C

Coal sample....	1		2		3		4		5		6		7	
	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct
CH_4	5.3	29.1	7.2	56.7	4.5	54.2	5.7	29.5	8.2	60.3	6.0	75.0	4.1	19.8
C_2H_4	1.2	6.6	1.0	7.9	.5	6.0	1.3	6.7	.7	5.1	.2	2.5	1.1	5.3
C_2H_6	.8	4.4	.6	4.7	.1	1.2	1.5	7.8	.6	4.4	.5	6.3	2.1	10.1
C_3H_6 / C_3H_8	1.3	7.1	.5	3.9	.3	3.6	2.1	10.9	.8	5.9	.2	2.5	2.3	11.1
Unidentified compound	-	-	-	-	-	-	-	-	-	-	Trace	-	-	-
$i\text{-}C_4H_{10}$	4.3	23.6	.8	6.3	.6	7.2	4.0	20.7	1.2	8.8	.5	6.3	3.7	17.9
$1\text{-}C_4H_8$	Trace	-	Trace	-	-	-	-	-	-	-	Trace	-	.6	2.9
$n\text{-}C_4H_{10}$	.2	1.1	Trace	-	Trace	-	.3	1.6	.2	1.5	Trace	-	.8	3.9
C_5H_{12}	5.1	28.0	2.6	20.5	2.3	27.7	4.4	22.8	1.9	14.0	.6	7.5	6.0	29.0
Total[1]	18.2	99.9	12.7	100.0	8.3	99.9	19.3	100.0	13.6	100.0	8.0	100.1	20.7	100.0

[1]Total hydrocarbon content of 1-ml sample.

TABLE 6. - Composition of hydrocarbon gases, minus 200-mesh fraction, 125° C

Coal sample.....	1		2		3		4		5		6		7	
	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct	Ppm	Pct
CH_4.....	6.8	21.2	4.6	31.5	4.7	36.2	3.2	22.9	4.7	31.5	3.8	50.7	4.7	29.7
C_2H_4.....	2.9	9.0	1.3	8.9	.9	6.9	1.2	8.6	.9	6.0	.7	9.3	.4	2.5
C_2H_6.....	3.8	11.8	.4	2.7	.3	2.3	1.0	7.1	.3	2.0	.8	10.7	.6	3.8
C_3H_6..... / C_3H_8.....	4.3	13.4	1.1	7.5	.5	3.8	1.3	9.3	.8	5.4	1.0	13.3	1.4	8.9
Unidentified compound.....	-	-	-	-	-	-	-	-	-	-	.2	2.7	-	-
i-C_4H_{10}.....	7.0	21.8	2.0	13.7	1.4	10.8	3.4	24.3	3.9	26.2	.6	8.0	2.1	13.3
1-C_4H_8.....	Trace	-	-	-	-	-	-	-	Trace	-	-	-	.9	5.7
n-C_4H_{10}.....	.8	2.5	.01	.1	Trace	-	.2	1.4	.1	.7	.2	2.7	.1	.6
C_5H_{12}.....	6.5	20.2	5.2	35.6	5.2	40.0	3.7	26.4	4.2	28.2	.2	2.7	5.6	35.4
Total[1].....	32.1	99.9	14.61	100.0	13.0	100.0	14.0	100.0	14.9	100.0	7.5	100.1	15.8	99.9

[1]Total hydrocarbon content of 1-ml sample.

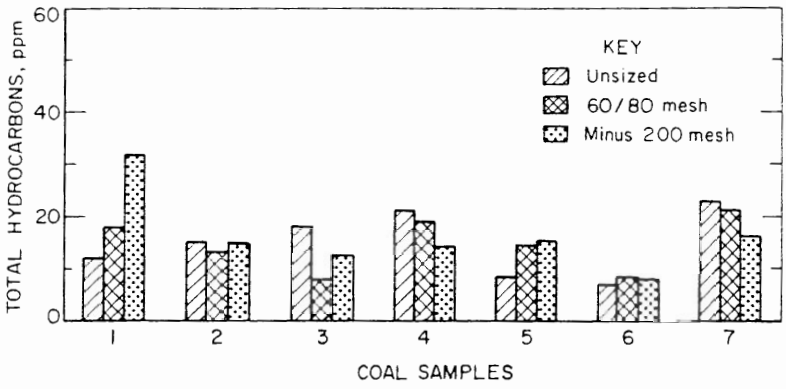

FIGURE 2. - Total hydrocarbons, 125° C.

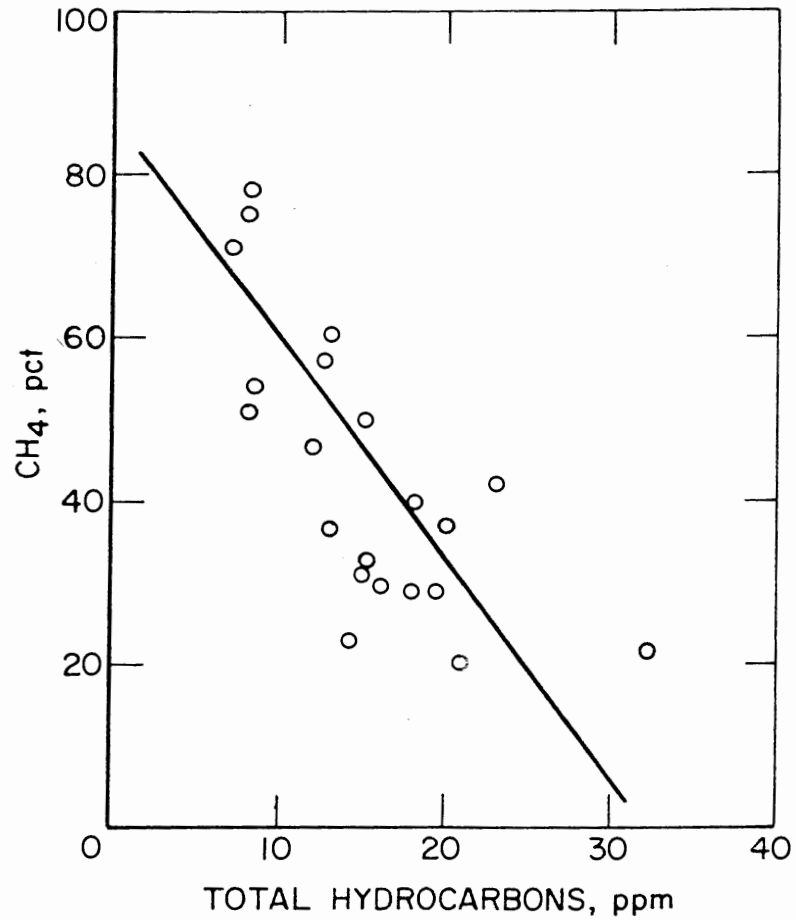

FIGURE 3. - Concentration of methane versus total hydrocarbons, 125° C.

For all samples the C_2 through C_5 hydrocarbons show a distinctive distribution of concentration versus carbon number. The average normalized distribution is shown in figure 4. Ethane, ethylene, and propane-propylene are present in approximately equal concentration. Of the C_4 isomers, the concentration of isobutane was 10 to 15 times greater than that of n-butane, and only one of the three C_5 isomers was detected. Isobutane and pentane were usually more abundant than any of the other hydrocarbons except methane. In coal sample 6, for the 60/80-mesh and minus 200-mesh fractions, trace amounts of an unidentified compound were also detected, and many of the samples produced a trace amount of 1-butene.

When the temperature of the oven was raised to 150° C, the hydrocarbon content of the gas increased by from 4 to 150 ppm (tables 7-9). Methane, isobutane, and pentane generally showed the greatest increase. The unidentified compound that eluted after the propane-propylene peak was found more frequently than at 125° C, but 1-butene was not detected at 150° C. The average normalized distribution of the total increase in hydrocarbons is shown in figure 5. Methane, isobutane, and pentane constitute over 75 pct of the total increase in hydrocarbons and

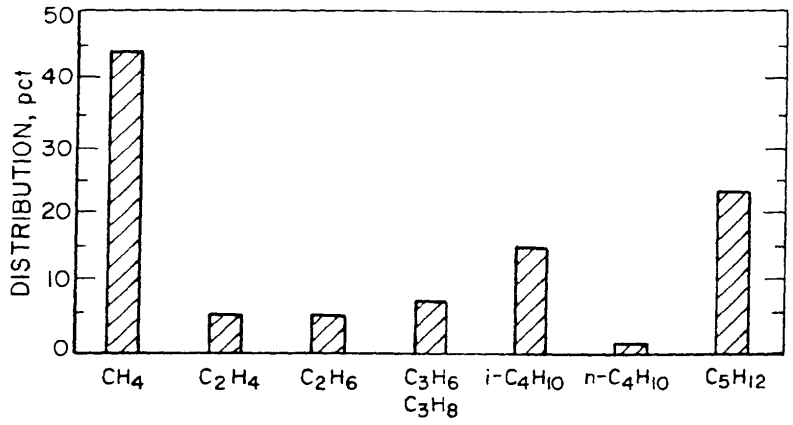

FIGURE 4. - Average normalized distribution of hydrocarbon gases, 125° C.

methane decreases with increased total hydrocarbons (fig. 6). Gases from coal samples 2 and 3 (Laramie seam, unsized) were not included in the calculations of the average change because over 90 pct of the exceptionally large increase in hydrocarbon content was pentane. For all other samples, the average increase was approximately equal for methane, isobutane, and pentane.

TABLE 7. - Hydrocarbon composition, unsized fraction, 150° C, ppm

Coal sample	1	2	3	4	5	6	7
CH_4	6.3	10.0	7.7	11.1	8.1	7.7	11.9
C_2H_4	1.3	3.0	2.0	3.8	1.3	.3	.6
C_2H_6	-	1.1	.7	1.8	.4	.9	2.5
C_3H_6 / C_3H_8	1.3	3.0	1.7	3.2	.5	.5	1.9
Unidentified compound	-	Trace	-	.2	Trace	-	-
$i\text{-}C_4H_{10}$	2.6	9.4	6.3	7.4	1.9	2.1	4.7
$1\text{-}C_4H_8$	-	-	-	-	-	-	-
$n\text{-}C_4H_{10}$	.2	.4	.1	.2	Trace	Trace	Trace
C_5H_{12}	4.2	122.0	149.4	6.4	3.3	2.0	6.9
Total[1]	15.9	148.9	167.9	34.1	15.5	13.5	28.5

[1]Total hydrocarbon content of 1-ml sample.

TABLE 8. - Hydrocarbon composition, 60/80-mesh fraction, 150° C, ppm

Coal sample	1	2	3	4	5	6	7
CH_4	10.2	8.6	7.4	11.8	10.7	9.6	10.4
C_2H_4	3.4	1.7	1.8	2.7	2.1	.7	2.1
C_2H_6	1.2	.8	.3	1.9	1.0	.6	2.9
C_3H_6 / C_3H_8	2.5	1.0	1.0	3.2	1.3	-	3.3
Unidentified compound	-	-	-	Trace	-	.2	Trace
$i\text{-}C_4H_{10}$	10.3	2.6	3.3	9.0	3.0	3.7	9.4
$1\text{-}C_4H_8$	-	-	-	-	-	-	-
$n\text{-}C_4H_{10}$	.4	-	.1	.6	-	-	-
C_5H_{12}	7.9	7.3	8.2	7.7	4.2	-	8.5
Total[1]	35.9	22.0	22.1	36.9	22.3	14.8	36.6

[1]Total hydrocarbon content of 1-ml sample.

TABLE 9. - Hydrocarbon composition, minus 200-mesh fraction, 150° C, ppm

Coal sample.....	1	2	3	4	5	6	7
CH_4.....	9.9	8.0	7.7	5.5	7.2	9.5	10.3
C_2H_4.....	3.7	2.5	1.8	2.7	1.3	1.9	5.3
C_2H_6.....	3.9	.7	-	1.3	.6	1.3	2.0
C_3H_6..... }	4.6	1.2	1.3	1.9	1.0	1.8	3.6
C_3H_8..... }							
Unidentified compound.....	-	-	Trace	Trace	-	1.6	1.9
$i\text{-}C_4H_{10}$.....	8.7	4.7	2.5	8.8	5.0	1.6	6.9
$1\text{-}C_4H_8$.....	-	-	-	-	-	-	-
$n\text{-}C_4H_{10}$.....	.9	.2	Trace	Trace	Trace	.7	.3
C_5H_{12}.....	7.2	9.4	7.8	7.5	4.5	1.0	7.7
Total[1].....	38.9	26.7	21.1	27.7	19.6	19.4	38.0

[1]Total hydrocarbon content of 1-ml sample.

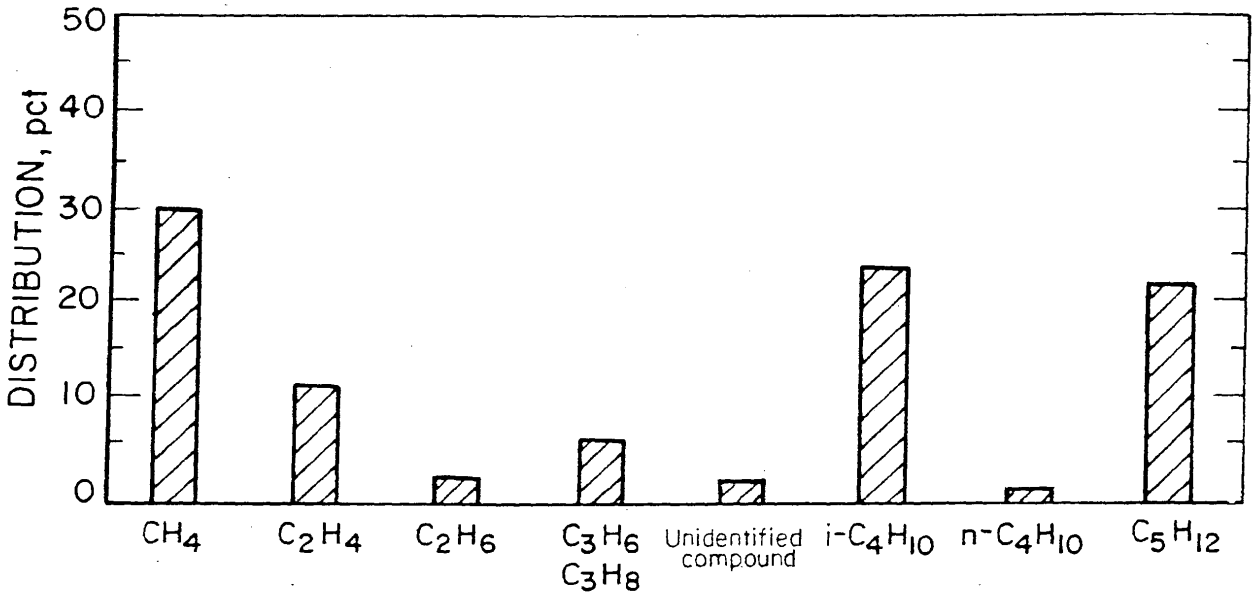

FIGURE 5. - Average normalized distribution of total increase in hydrocarbon gases, $\Delta T = 125°$ to 150° C.

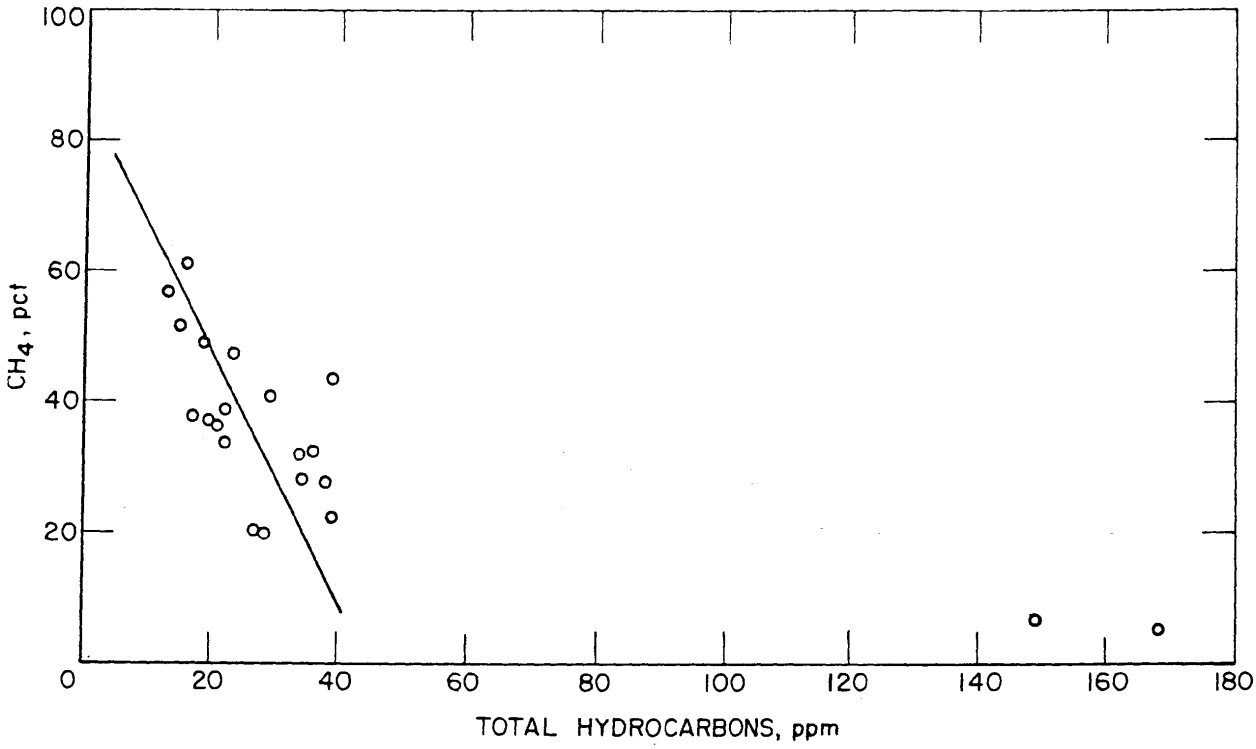

FIGURE 6. - Concentration of methane versus total hydrocarbons, 150° C.

DISCUSSION

Although the total amount of gases derived from the coal samples was small, (16 to 60 ppm total hydrocarbons per gram of coal), the relative composition of the gases was significant. At 35° C, the gas was primarily methane. At 125° C, methane composed less than 50 pct of the hydrocarbon gas. In order of decreasing concentration, the components of the gas were methane, pentane, isobutane, propane-propylene, ethane, ethylene, trace amounts of 1-butene, and an unidentified compound.

When the temperature of the oven was raised from 125° to 150° C, the amount of hydrocarbon gases increased (fig. 7). As at the lower temperature, difference in total hydrocarbons with particle size were not large. Averaged over all samples except 2 and 3 unsized, methane, isobutane, and pentane constitute over 75 pct of the total increase in hydrocarbons. Samples 2 and 3 unsized, which came from different mines in the same seam, showed an exceptionally large increase in the amount of pentane released at 150° C, although the concentration of pentane at 125° C did not differ significantly from that of other samples.

The retention time and peak shape of the unidentified compound listed between propane-propylene and isobutane indicates that it is a low-molecular-weight hydrocarbon, probably not acetylene, possibly propyne ($HC{=}CCH_3$) or 1, 2 propadiene ($H_2C{=}C{=}CH_2$), which have the same molecular weight and similar boiling points. It is also possible that the compound is an alcohol or some

other organic compound. Similarities in molecular weight and boiling points in addition to the small amount of the compound available, makes positive identification difficult.

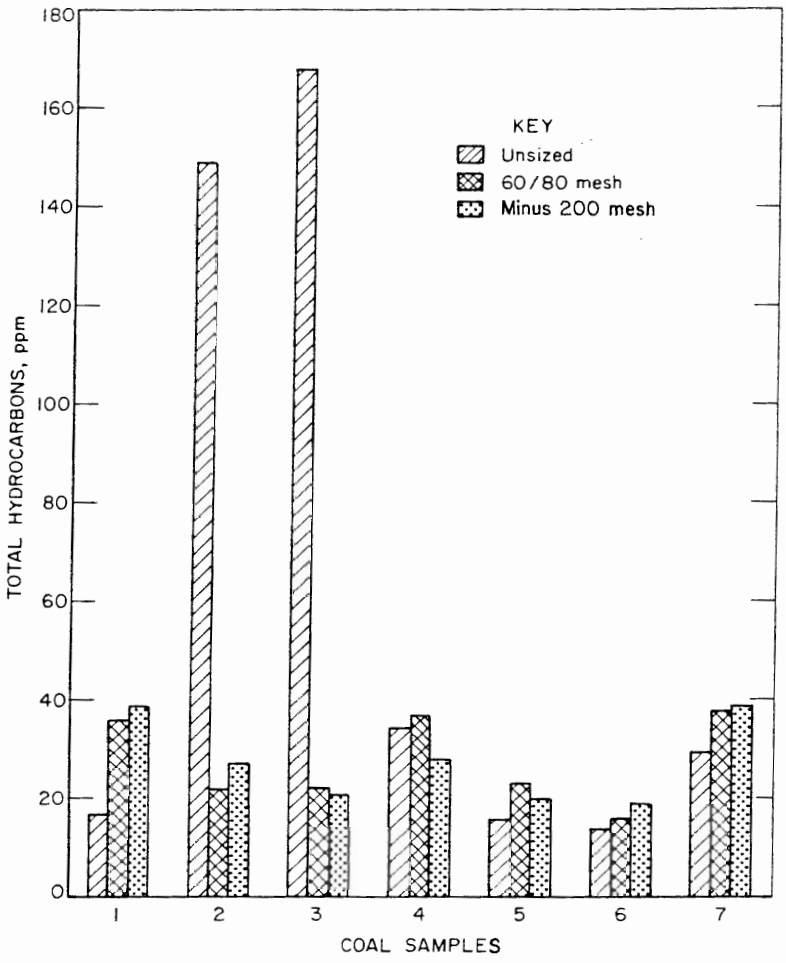

FIGURE 7. - Total hydrocarbons, 150° C.

At 125° C, traces of 1-butene were found consistently, but it was not detected in any of the gas samples at 150° C. The disappearance of the 1-butene peak in conjunction with the increase in n-butane suggests that 1-butene could react with hydrogen to form n-butane. At 125° C the rate of formation may be slightly greater than the rate of conversion to n-butane, whereas at 150° C the rate of conversion is greater than the rate of formation or desorption of 1-butene.

Only one C_5 isomer was detected. Because of the small differences in gas chromatographic retention time, whether the compound is isopentane, neopentane, or n-pentane cannot be determined in this experiment. Therefore, it is listed only as pentane (C_5H_{12}).

At both temperatures, changes in hydrocarbon concentration with time were relatively small and not consistent, apparently affected by the concentration of CO_2 formed by oxidation of the coal. The distribution of the hydrocarbons was not time-related. Previous analyses of coal gases have not indicated high concentrations of the C_4 and C_5 compounds, nor have they shown a preferred isomer.

The distribution of gases does not correspond to the boiling points or heats of formation of the hydrocarbons (table 10). If hydrocarbon gases are formed during the experiment by dissociation of a large aliphatic chain into shorter hydrocarbon fragments, it may be assumed that the amount of each hydrocarbon should increase with decreased heat of formation. Although dissociation of coal is believed to occur readily during low-temperature carbonization, it has been suggested that even the large tar molecules produced during carbonization are desorbed out of the micropore structure rather than formed from the coal (46).

TABLE 10. - Boiling point and heats of formation of hydrocarbon gases[1]

Hydrocarbon	Boiling point, ° C	ΔH_f, kcal/mole
CH_4 (methane).....	-164	-17.89
C_2H_4 (ethylene).....	-103.7	12.50
C_2H_6 (ethane).....	- 88.6	-20.24
C_3H_6 (propylene).....	- 47.4	4.88
C_3H_8 (propane).....	- 42.1	-24.82
1, $2C_3H_4$ (1,2 propadiene)	- 34.5	45.92
C_3H_4 (propyne).....	- 23.2	44.32
i-C_4H_{10} (isobutane).....	- 12	-31.45
1-C_4H_8 (1-butene).....	- 6.3	.28
n-C_4H_{10} (n-butane).....	- .5	-29.81
neo-C_5H_{12} (neopentane)...	9.50	-36.38
i-C_5H_{12} (i-pentane).....	27.9	-36.38
C_5H_{12} (pentane).....	36.1	-35.00

[1]Weast, R. C. (ed.). Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio, 54th ed., 1973-74, pp. C75-C542, D76.

Comparing the distribution of gases with their heats of adsorption on carbon black (table 11) gives a slight indication that desorption may be a significant process during the experiment. In most determinations of limiting isosteric heats of adsorption on carbon black, differences for ethane-ethylene (0.2 kcal/mole) and propane-propylene (0.03 kcal/mole) are small, indicating that these compounds would desorb at approximately the same rate. There is a larger difference in the heats of adsorption of the C_4 isomers (0.5 kcal/mole), with isobutane having the lower heat of adsorption. Heats of adsorption for the C_5 isomers vary a total of 1.8 kcal/mole, in the order neopentane<isopentane<n-pentane, indicating that neopentane may be more readily desorbed. However, the complete absence of two pentane isomers cannot be explained by differences in the heat of adsorption. Since the heat of adsorption increases with carbon number, desorption does not explain the predominance of C_4 and C_5 hydrocarbons.

Whether the hydrocarbon gases were formed or desorbed during the experiments cannot be determined from the data obtained. If they are desorbed from the coal, the gases then must have been formed in some previous stage of coalification. Determining the mechanism (s) of hydrocarbon evolution at low temperatures is beyond the scope of this experiment.

TABLE 11. - Heats of adsorption (Q_1) of hydrocarbon on carbon black, kcal/mole[1]

Adsorbate	di Corcia[2]	Hoory[3]	Ross[4]	Kalashnikova[5]
CH_4	-	3.020	3.13	3.11
C_2H_4	-	4.390	4.40	4.30
C_2H_6	4.70	4.600	3.78	4.53
C_3H_6	-	5.900	-	-
C_3H_8	5.90, 6.10	5.870	6.26	5.93
$i\text{-}C_4H_{10}$	6.80, 6.95	6.910	-	6.95
$n\text{-}C_4H_{10}$	7.35, 7.54	7.450	8.10	7.21
$1\text{-}C_4H_8$	-	-	-	6.95
$neo\text{-}C_5H_{10}$	-	-	-	6.85
$i\text{-}C_5H_{12}$	-	-	-	8.04
$n\text{-}C_5H_{12}$	8.41, 8.43	-	8.61	8.67

[1]For purposes of discussion it is assumed that heats of adsorption on carbon black and coal are similar, even though coal is known to be a less homogeneous adsorbent. It is also assumed that adsorption is a reversible process with the heat of desorption equal to minus the heat of adsorption.

[2]di Corcia, A., and R. Samperi. Hydrogen-treated Graphitized Carbon Black. Limiting Isosteric Heats and Entropy Charges Upon Asdorption of Hydrocarbons. J. Phys. Chem., v. 77, 1973, pp. 1301-1306.

[3]Hoory, S. E., and J. M. Prausnitz. Adsorption of Hydrocarbons on Graphitized Carbon. Trans. Faraday Soc., v. 63, 1967, pp. 455-460.

[4]Ross, S., J. K. Saelens, and J. P. Olivier. On Physical Adsorption XVIII. Limiting Isosteric Heats of Adsorption of Gases on Graphitized Carbon by the Chromatographic Method. J. Phys. Chem., v. 66, 1962, pp. 696-700.

[5]Kalashnikova, E. Va., A. V. Keselev, R. S. Petrova, and K. D. Scherbokova. (Gas Chromatographic Investigation of the Adsorption Equilibrium or Graphitized Thermal Carbon Black. I. Henry Constants and Heats of Adsorption of C_1 - C_6. Hydrocarbons at Zero Coverage.) Chromatographia, v. 4, 1971, pp. 495-500.

SUMMARY

Although it could not be determined if the gases were being desorbed or formed, the data obtained from this experiment show that in addition to methane, most of the C_2 through C_5 hydrocarbons are formed during coalification. Of the C_2 through C_5 compounds, isobutane and one of the pentane isomers are apparently formed more readily than other hydrocarbons. This indicates that the mechanisms by which hydrocarbon gases are produced during coalification are more complex than simple demethanation.

This experiment has shown that it is possible to study gas evolution from coal in reasonably short periods of time at temperatures below 200° C; however, to obtain accurate results, such experiments should be performed in a closed, oxygen-free system, preferably in an inert atmosphere at a controlled pressure. More elaborate experiments, more expensive in terms of time and equipment, are necessary to obtain additional information about the formation of hydrocarbon gases in coal.

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